

THE DIRECT DETERMINATION OF ORGANIC SULFUR IN RAW COALS

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INTRODUCTION

The sulfur content among coals varies to some degree in total quantity and in the forms present. Generally, the forms of sulfur in coals are the inorganic (sulfide and sulfate) and the organic (a complex mixture of organo types). The sulfate content is usually present in low amounts except in some instances where weathering has converted some of the pyrite to sulfate. The sulfide form can occur as the minerals pyrite and marcasite in a rough size range from 0.25 to 200 micrometers.

The organic sulfur in coals is intimately bound to the coal molecule and is difficult to determine directly when other forms are present. The organic sulfur content in most american coals range from about 0.5 to 3%.

A total sulfur analysis will give the information on whether present SO₂ emission standards will be met upon combustion of the candidate coal. If the total sulfur is too high, and stack gas cleaning is not available, some form of desulfurization is required before this energy source can be used. Cleaning processes can remove varying amounts of the inorganic forms, and some organic sulfur may also be extracted, but for all intents, the content of this latter form may be regarded as the lower level at which coal can be beneficiated. Therefore, the baseline level of organic sulfur is important to know so that economic and time effective inorganic sulfur extractions can be applied which in turn can comply with combustion standards.

Current ASTM methods provides for the direct analyses of the total, sulfate, and sulfide sulfurs. The accepted techniques for determining the sulfur forms in coals are the ASTM⁽¹⁾ standard wet methods. The total sulfur is determined by the Eschka method (D3177-75) and the sulfate and sulfide by selective acid leaches (D2492-68). The organic sulfur is then obtained from the difference of the total and the two inorganic forms since no reliable direct method is available. The possible accumulation of errors and the time required (~1 1/2 days) to obtain the organic sulfur by difference has made this approach undesirable but necessary.

The precision of the organic sulfur value obtainable from this approach was calculated from numerous analyses at BMI in conjunction with precision estimates of the respective ASTM methods. At two standard deviations (95 confidence level) the precision was found to be $\pm 25\%$.

Instrumental methods also can be used to determine the inorganic forms and total sulfur for an estimation of the organic sulfur content. The two methods use X-ray analyses on pressed pellets of pulverized coal. In one, Hurley & White⁽²⁾, use X-ray fluorescence to characterize for all of the sulfur forms by wavelength shift of the SK_α peak caused by variation in the sulfur bonding. The second⁽³⁾ is discussed in an unpublished report on sulfur determination in coals, and utilizes X-ray fluorescence for total and sulfate sulfurs and X-ray diffraction for sulfide sulfur. Organic sulfur is obtained by the difference in the latter technique.

Both of the X-ray methods agree with corresponding wet chemical data on the same samples. The precisions of these instrumental methods therefore, are at least as good as the ASTM procedure but the time of analyses is reduced to several hours. A direct method for determining organic sulfur in coals was reported by Sutherland⁽⁴⁾ using the electron microprobe on pressed pellets of coal.

A BMI supported program, therefore, was initiated to develop a direct and specific method for determining the organic sulfur content in coals and in the presence of the other sulfur forms. The approach taken entailed the low temperature reaction of ionized oxygen species with raw coals to yield volatile SO_x components which are the reaction products with the organic sulfur content of the coals. The SO_x products can be collected in a suitable trap maintained at low temperatures and subsequently analyzed.

Equipment

For this purpose, the instrument used for the oxidation of coals during this program was the LFE LTA 600L low temperature asher. The generator operates at a crystal controlled frequency of 13.56 MHz and has an output capable of delivering 300 watts of continuously variable power distributed among five separate reaction chambers. Normal ashing is carried out under continuous rough (300 l/m capacity) so as to maintain a pressure of 1 torr at an oxygen input flow of about 50 cc/min. The low temperature oxidation technique has been used to study the mineral matter content of coals. As indicated previously, the technique utilizes the oxidative properties of the reactive ionic and atomic species of oxygen which are produced when molecular oxygen is passed through a high frequency field. The ionized oxygen species are directed to the surface of the raw coal where selective oxidation of the organic content leaves the mineral matter relatively unaltered for study. The reaction produces volatile oxides of the total organic content. These products are CO , CO_2 , H_2O , SO_x , and NO_x , and they are normally allowed to be discharged through the vacuum pump. The temperature of the coal surface reaction under these conditions can vary from 50 to 300°C depending primarily upon the power applied to the RF coils. Frazer et al⁽⁵⁾ and Mitchell et al⁽⁶⁾ used low temperature ashing of coals to study mineral stability under a variety of conditions. Although better stability of minerals were observed than that shown by the air oxidation method at 400°C, however, it was noted that pure pyrite could be oxidized at the high temperatures, 200-300°C.

To provide for the collection facility of the desired vapor species, the exit of one of the reaction chambers was rerouted to accommodate a glass trapping system. This modification is shown schematically in Figure 1. The all glass assembly, with ball joint connectors includes a stop cock (D), a trap (C) to collect the oxidized species and a connector at (E) to either evacuate during a run or to attach a gas bubbling trap for collecting the SO_2 at the end of a run. The remaining chambers were left intact so as not to interfere with the operation of the instrument.

Figure 2 shows the sample holder used for loading the sample for the oxidation run. Sample plate (A) is placed into the holder as shown after loading with coal. The sample holder containing the sample is inserted in the modified sample chamber. This overall arrangement provides ease of handling of the sample.

Reaction and Collection Procedure

A weighed sample is loaded into the sample holder onto a glass plate. The sample holder is inserted into the reaction chamber (A) through part B. The system is carefully evacuated to about 0.2 torr. As the oxidation of the coals progress, the temperature (-196 C) and pressure (1 torr) conditions permit trapping of the SO₂ and SO₃ gases as solids.

The generator is turned off after, upon visual examination, the samples appear to be completely oxidized. The oxidation time can vary from 1 to 3 hours. Helium is slowly admitted through stop cock (D) until the system can be opened to the air. A glass impinger bottle containing about 50 cc of 3% H₂O₂ solution is attached to (E). With a slow purge of He through the trap and impinger, the Dewar is removed to permit the transfer of the condensed SO₂ into the peroxide scrubber. The trap is then rinsed with a peroxide solution to collect the SO₃ component of the product. The two solutions are combined for sulfate analyses using the Dionex Mod 10 Ion Chromatograph.

Samples

The coals which were selected for this program were used as received except that they were ground to pass -200 mesh sieve (74 μ m). Wet chemical sulfur analyses were obtained on these coals. In addition to a reproducibility study on one coal, several other coals of varying sulfur and ash contents were run to establish the suitability of this method to coals possessing varying chemical contents. The candidate coals are listed in the Table 1. along with their pertinent makeup.

The amount of coal samples taken for these runs were in the 20-30 milligram range. The resulting sulfur collections were expected to be of sufficient quantity to be determined by the analytical method to be used. Small charges were used in efforts to reduce the oxidation time to several hours. After the initial surface of coal is removed, the penetration of the ionized oxygen to the coal underlying the ash is time dependent. The possible errors introduced in the overall determination of organic sulfur due to macroscopic inhomogenities accentuated by the small sample charges could be evaluated in the precision series.

TABLE 1. SAMPLES USED IN LOW TEMPERATURE OXIDATION STUDIES

| Sample Coal | Sulfur, % | | | | Ash, % | Moisture |
|--------------------------------|-----------|---------|---------|---------|--------|----------|
| | Total | Pyritic | Sulfate | Organic | | |
| 719-2 (Ohio) | 6.3 | 1.58 | 2.74 | 1.9 | 14.2 | 3.5 |
| 719-3 (Ohio) | 5.2 | 3.6 | 0.07 | 1.4 | 17.1 | 1.2 |
| Hazard #4 (Kentucky) | 1.52 | 0.66 | 0.04 | 0.82 | 12.8 | 1.1 |
| Colstrip #2 (Western) | 0.68 | 0.18 | 0.14 | 0.36 | 9.0 | 16.0 |
| Beach Bottom #1 (W.Va.) | 1.97 | 1.35 | 0.03 | 0.59 | 25.1 | 1.7 |
| <u>Organic Compounds</u> | | | | | | |
| Dithiopropionic | 17.7 | 0 | 0 | 17.7 | 0 | - |
| 2-Thiophene Carboxylic Acid | 24.7 | 0 | 0 | 24.7 | 0 | - |

The pure organosulfur compounds shown were also run since the results would represent ideal recovery experiments in the absence of interfering mineral forms. The sample charges used for these runs were in the 5-10 milligram range.

A study was also made of the stability of FeS_2 under the ashing conditions for coal. Oxidation of this compound yields volatile SO_2 which would be indistinguishable from that derived from the organic sulfur in coal. In addition, the pure FeS_2 was also mixed with other components to assess their affect upon its conversion. These materials include pure SiO_2 , graphite, ash, and coal.

EXPERIMENTAL RESULTS

Oxidation Study of FeS_2

It was first necessary to establish conditions which prevented or reduced considerably the oxidation of pyrite to yield SO_x . The experimental conditions which were varied for the FeS_2 study included applied power to the plasma, oxygen flow, position of samples in relation to the plasma, particle size of FeS_2 , and mixtures of various materials with pure FeS_2 . For the runs with only FeS_2 , it appears that the conversion to Fe_2O_3 and volatile SO_2 occurs under any condition. However, the severity of conversion increases directly with the applied power and inversely with particle size. The position of the sample in the chamber and the rate of oxygen flow used has minimal, if any, affect upon the oxidation of FeS_2 .

The runs made using mixtures of FeS_2 with the listed additives produced mixed results. It was found that by adding graphite, SiO_2 , or an organic sulfur compound to pure FeS_2 did not prevent the FeS_2 reaction with oxygen. However, admixtures with coal or fly ash appears to prevent FeS_2 oxidation. The reason for the apparent inhibition of the reaction is not known but seems to be associated with characteristics of the ash other than SiO_2 . The presence of the natural ash in coals accelerates the reaction of the organic phase with the plasma. In samples containing no ash, such as graphite or an organosulfur compound, the reaction with ionized oxygen is slower.

Coal Studies

Coals were oxidized using the optimum instrumental conditions as determined to be suitable for the pyrite studies. These were found to be (1) applied power of 150 watts overall (30 watts/chamber); (2) oxygen flow at 30 cc/min; (3) and a pressure of 1 torr. The sample charge of about 25 milligrams was used. The collected sulfates were determined on a Dionex Model No. 10 Ion Chromatograph.

Using the above conditions for a coal (719-2), a series of ten runs supplied a measure of the repeatability of this technique for the organic sulfur recovery in one coal. These recovery data and precision are shown in Table 2. The ratio of the obtained/expected values allow for the calculation of the relative standard deviation of 19% at the 95% confidence level. This is slightly better than that achievable by the indirect ASTM method.

The repeatability data shown in Table 2 includes a wide range of variables. These include (1) possible inhomogeneity of small coal charges, (2) ability to duplicate reaction and collection techniques, (3) analyses of sulfate solutions, and (4) runs extended over a period of several weeks.

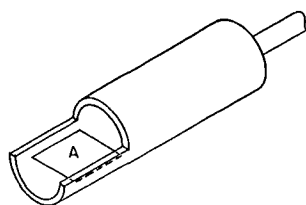


FIGURE 2. SAMPLE PLATE AND HOLDER INSERT

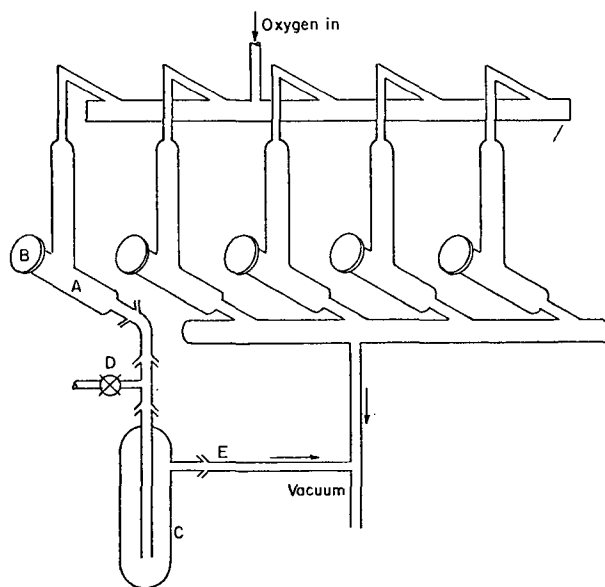


FIGURE 1. SCHEMATIC OF LOW-TEMPERATURE ASHER SHOWING MODIFIED REACTION CHAMBER AND GAS FLOWS

TABLE 2. REPEATABILITY RUNS OF THE ANALYSES OF ORGANIC SULFUR FROM OXIDATION OF 719-2 COAL

| Net Organic Sulfur, micrograms | | Ratio Obtained/Expected |
|--------------------------------|----------|-------------------------|
| Expected | Obtained | |
| 440 | 450 | 1.023 |
| 405 | 410 | 1.012 |
| 420 | 475 | 1.131 |
| 420 | 360 | 0.861 |
| 380 | 360 | 0.949 |
| 430 | 450 | 1.047 |
| 440 | 440 | 1.00 |
| 415 | 380 | 0.916 |
| 430 | 350 | 0.814 |
| Mean | | 0.971 |
| % SD (95%) | | 19.0 |

The second study involving coal 719-2 was to oxidize for SO_x recovery after spiking with quantities of FeS_2 in a particle size range of $<37 \mu\text{m}$. The sulfide was premixed with coal at about the 12% level so that the charge to be oxidized was about 25 milligrams of coal and 3 milligrams of pure pyrite. The mix runs were similar to the coal-only runs for the overall procedure. Results of the coal- FeS_2 runs are shown in Table 3. The relative standard deviation at the 95% confidence level is seen to be 17%.

TABLE 3. ANALYSES OF ORGANIC SULFUR FROM OXIDATION OF 719-2 COAL SPIKED WITH PURE FeS_2

| Organic Sulfur, micrograms | | Ratio Obtained/Expected |
|----------------------------|----------|-------------------------|
| Expected | Obtained | |
| 350 | 330 | 0.943 |
| 345 | 350 | 1.014 |
| 370 | 440 | 1.190 |
| 300 | 320 | 1.07 |
| Mean | | 1.054 |
| % SD (95%) | | 17.0 |

The third major experiment involved the repeatability of this technique when applied to a wide range of coals. The basis for selection included a variation in total, pyritic, and organic sulfurs as well as the ash content. The coals used for these runs are listed in Table 1.

The four coals were run in triplicate using similar procedure conditions as the two previous studies with coal 719-2. The results on the four coals are shown in Table 4. One run (colstrip) appears to be out of line, but the other ratio data seem to be well within the errors associated with either the ASTM or this direct method. The results show that this direct (oxidation)

method does provide a reasonable estimate of the organic sulfur content in a variety of coals.

Theoretical recoveries of S in pure organic compounds were the 90-95% range. The melting points of the two organo sulfur components are near the temperatures achieved during the oxidations. It is uncertain what, if any, affect this has on full recoveries.

TABLE 4. APPLICATION OF THE OXIDATION TECHNIQUE TO VARIOUS COALS

| | Organic Sulfur, micrograms Expected | Obtained | Ratio | General Constituent Range |
|-----------------|--|----------|-------|-----------------------------------|
| Colstrip #2 | 77 | 123 | 1.6 | Low pyrite, OS, Ash |
| | 75 | 85 | 1.1 | |
| | 70 | 80 | 1.1 | |
| Hazard #4 | 220 | 173 | 0.79 | Medium pyrite, OS, Ash |
| | 185 | 173 | 0.94 | |
| | 200 | 100 | 0.95 | |
| Coshocton 719-3 | 330 | 300 | 0.91 | High pyrite and OS, medium ash |
| | 330 | 313 | 0.95 | |
| | 325 | 340 | 1.05 | |
| Beach Bottom #1 | 180 | 195 | 1.1 | High pyrite and ash, medium OS |
| | 185 | 210 | 1.1 | |
| | 170 | 190 | 1.1 | |

Discussion of Problems

Other oxidized products of coals were condensed at the liquid nitrogen temperatures. Although no attempts were made to analyze the full contents of the condensed material, small amounts of ozone were present in most runs. Accidental leaks in the system during a run appears to deplete not only the ozone, but also the condensed SO_2 . The resulting NO_x apparently reacts with SO_2 to form a NO-SO complex which makes it unavailable for the analytical method used.

The condensed SO_2 is reasonably stable at the trap temperature and pressure used to carry out the oxidation. The calculated loss through vaporization is about 40 nanograms per hour.

Other SO_x collection techniques were tried in efforts to simplify its recovery for analysis. One attempt included the possible catalytic conversion of SO_2 to SO_3 for its lower temperature collection. Poisoning of the platinum surface occurred about half way through the run to make this approach unsuccessful. The second attempt involved placing a NaOH-laden quartz wool plug in the rear of the holder insert. This appears to be very effective in capturing the SO_x vapor. However, to be effective the plug should be slightly moist, and this introduces some vacuum problems which have not been studied too thoroughly.

Predeposition of SO_3 (probably as H_2SO_3 or H_2SO_4) on the walls of glass system can occur at high SO_x concentrations. The deposition on the glass surfaces was very much in evidence in the investigations with pure FeS_2 . Blank levels were found after coal runs.

CONCLUSIONS

Based upon the experimental work carried out on this program, a direct method for determining the organic sulfur content in coals has been developed. The procedure makes use of the relative ease of oxidation of the organically bound component of coals with ionized plasma of oxygen to yield volatile oxidic species peculiar to the total organic makeup. The desired products are condensed at a low temperature for subsequent analysis.

The work reported herein has demonstrated that this technique is specific for the organic sulfur content of coals within the error of the overall procedure. Repeatability runs on one coal (719-2) has produced relative standard deviations better than those obtained for organic sulfur using the different methods of ASTM. Similar precision was obtained from the same coal even when spiked with comparatively large quantities of pure FeS_2 in the particle size range of $<37 \mu\text{m}$. No sacrifice in the recovery amounts of the expected organic sulfur in the coal were indicated in these spiked runs. Successful application of this technique to other coals of varying constituents has provided some measure of the ruggedness and confidence of this approach. Also the repeatability runs indicate that the use of the 25 milligram sample charge is justified. Any error which may arise from the inhomogeneous distribution of organic sulfur in the use of small charges appears to be minimal or within the experimental precision of the method.

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